



(Source: <http://www.chem.rochester.edu/~chem421/polymod2.htm>)

Chem 421: Introduction to Polymer Chemistry

The Chemistry of Photoresists

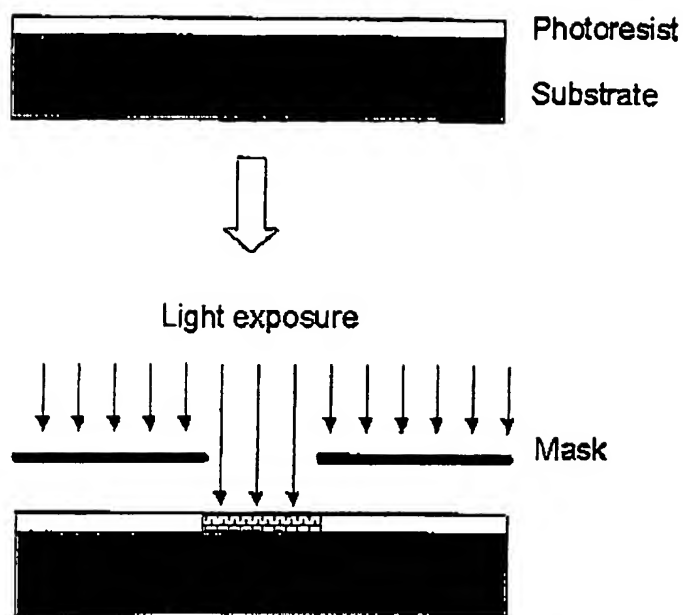
General Principals

Photoresists have enabled the modern electronic revolution. The patterns of conductors on circuit boards and the tiny transistors on microchips are "printed" using photoresists. The technology of photoresists has been refined to the point where many millions of micron-sized devices can be fabricated simultaneously and reliably on silicon substrates. Research on yet smaller (and therefore more dense and efficient) circuitry continues apace today.

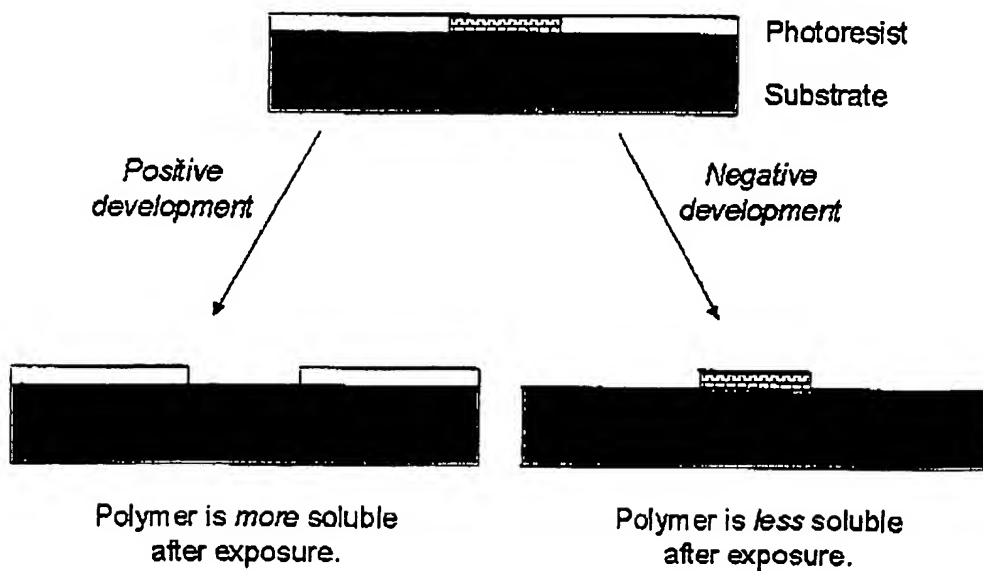
The story of photoresists is largely one of *polymer modification chemistry*. All photoresists are polymeric coatings that are designed to change properties upon exposure to light. Then, either the exposed or unexposed regions of the coating can be selectively removed to reveal the substrate beneath. The second role of the photoresist is to "resist" the actual circuit formation step, i.e. etching, ion implantation, metal deposition, etc., thereby protecting the substrate beneath where required. In most cases, the process is repeated many times to produce the final, complicated pattern of circuitry.

Photoresist Processing

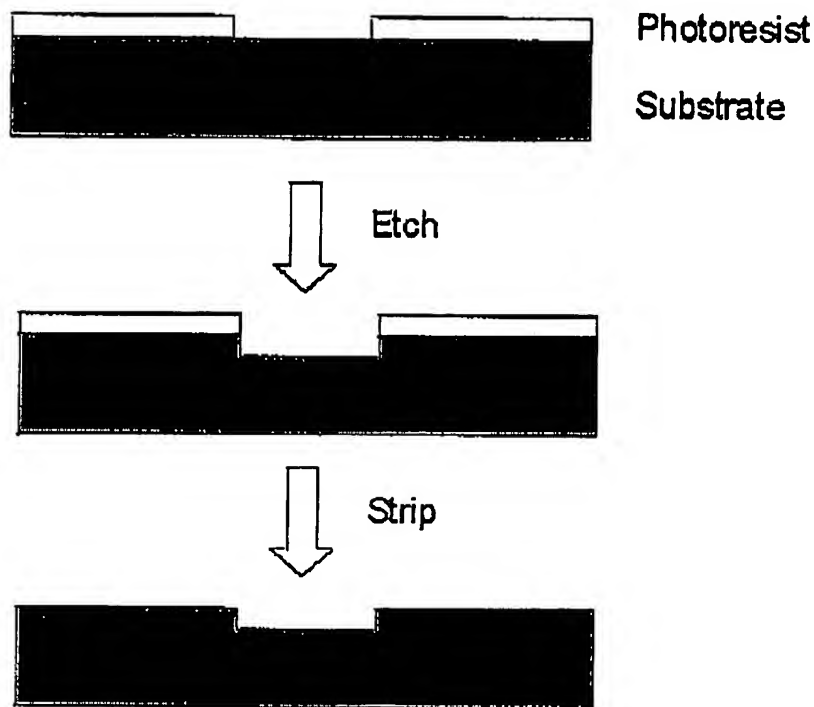
The process begins by covering the whole substrate surface with a thin layer (ca. 1 micron) photoresist material, usually by *spin-coating*. The coating is then selectively irradiated with light (usually UV) through a stencil, or *mask*, that is designed to allow light to fall only on desired places.



The light causes a chemical change in the exposed region. Depending on the system, it is possible to wash away either the exposed or unexposed regions selectively, using the appropriate fluid, called the *developer*. When the exposed region is removed by the developer (i.e., exposure makes the photoresist more soluble), the process is called *positive tone*, and when the developer leaves the irradiated region behind (i.e., irradiation makes the photoresist less soluble), the process is called *negative tone*.



In the final step, some kind of process is applied to the revealed substrate. In the example shown below, a chemical treatment etches away some of the substrate, while the photoresist protects the other regions. (Alternatively, metal deposition, ion implantation, or other processes can be carried out.) Finally, an appropriate reagent removes (*strips*) the remaining photoresist, and the substrate is ready for the whole process to be repeated for the next stage of circuit fabrication.



The Chemistry of Photoresists

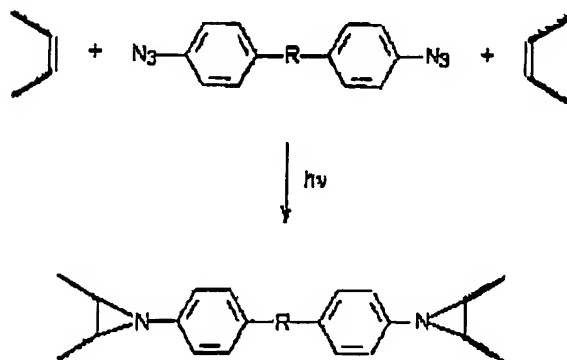
There are numerous polymer systems that have been applied to photoresist technology. Below are presented a few selected examples among many.

Photoresists continue to be an active area of research for polymer chemists, as devices of ever smaller sizes are pursued.

Bisazide crosslinking

The earliest photoresists were based on the photocrosslinking of "cyclized rubber" using an additive that contained two azide groups. (Cyclized rubber is obtained by acid treatment of poly(*cis*-isoprene), a process which leads to some ring formation in

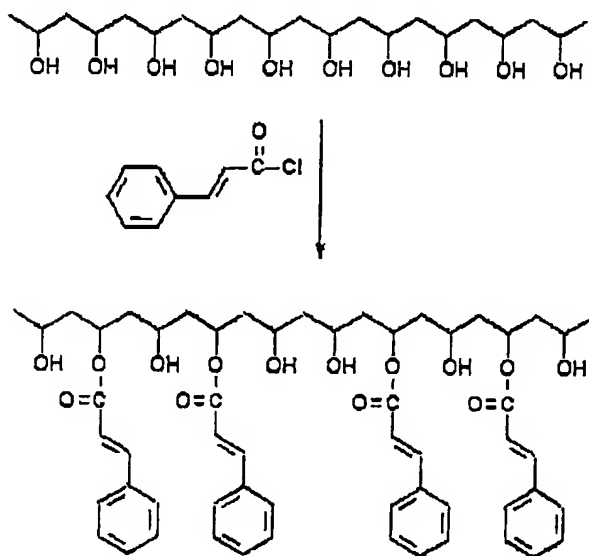
the polymer, and stiffens it, thereby raising its T_g .) When the bis-azide is photolyzed, it extrudes nitrogen and produces two very reactive nitrene moieties. The nitrenes can form bonds with the cyclized rubber in a variety of ways, the most common of which is aziridine ring formation, as shown.



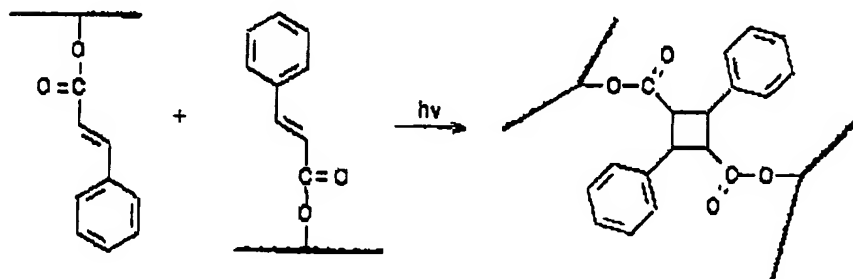
Naturally, these reactions lead to crosslinking of the polymer, and it becomes less soluble, ready for negative development.

Poly(vinyl cinnamate)

Another interesting negative tone photoresist is poly(vinyl cinnamate). This polymer is synthesized by the partial esterification of poly(vinyl alcohol), which itself is made by a polymer modification reaction (hydrolysis of poly(vinyl acetate)).

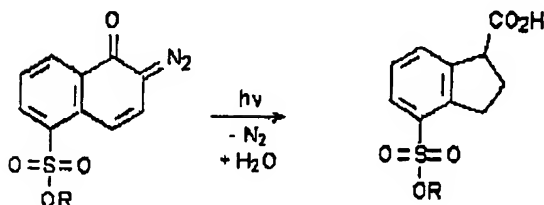
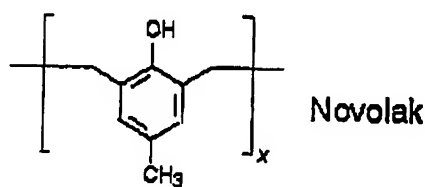


The cinnamate groups undergo [2+2] cycloaddition when irradiated, leading to a crosslinked polymer suitable as a negative tone photoresist.



Novolaks

Novolaks are phenol-formaldehyde type polymers, generally synthesized using cresol rather than phenol, with the polycondensation reaction halted before the polymer becomes crosslinked. Being phenols, these polymers are soluble in aqueous base, although the rate of dissolution is quite slow. However, in the presence of suitable additives, the dissolution process can be greatly enhanced. The additives can be produced photochemically, leading to a useful photoresist system. In fact, Novolaks have been the "workhorse" photoresists of the modern microelectronic revolution. The photoresist consists of Novolak polymer, with a small amount of diazonaphthaquinone dissolved in it. When irradiated, the diazonaphthaquinone undergoes the *photochemical Wolf rearrangement*, which eventually produces a carboxylic acid.



Diazonaphthaquinone additive

Of course, the carboxylic acid (produced by irradiation) is even more soluble in base than the Novolak itself. Its presence increases the rate of dissolution of the coating by *orders of magnitude*. Therefore the unirradiated regions are effectively insoluble, leading to a *positive tone photoresist*. The exact reason for the increased dissolution rate is not yet understood, and remains a matter of contention and research. Nevertheless, this system works well, and can produce very intricate features, as shown below.



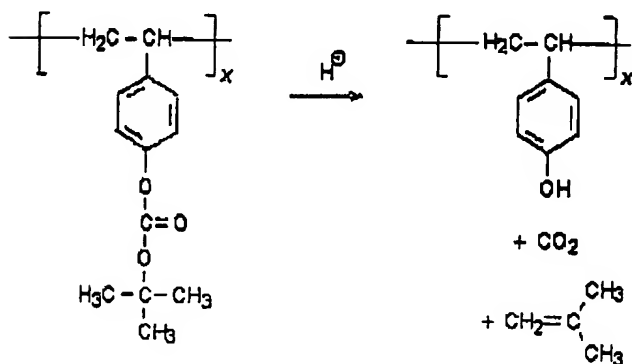
Chemically Amplified Photoresists

While the Novolak photoresists provide excellent performance, there is always room for improvement. One aspect that was addressed through clever polymer modification chemistry was the amount of light required to produce sufficient enough chemical change for development. That is, if the amount of light exposure, or *dosage*, required could be lessened, the whole process could be carried out faster.

Collaborative work between IBM (especially C. Grant Winson, now at Univ. of Texas Austin) and Prof. Jean Frechet (then at Univ. Ottawa, now at Berkeley) resulted in the invention of the concept of *chemically amplified photoresists*. In this system, exposure to light creates a *catalyst* for another chemical reaction. The second chemical reaction is responsible for the change in solubility needed for development. The essence of chemically amplified photoresists is that one photon can lead to many secondary reactions, therefore the available light is used very efficiently. (Quantum yield is much greater than 1.)

The most well known system of this kind is based on *t*-Boc-styrene polymer. Simply put, this polymer contains phenolic groups protected with *t*-Boc groups. In the

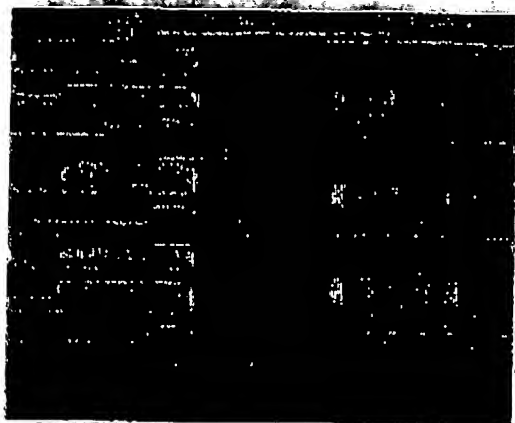
presence of acid catalyst, the protecting groups decompose to carbon dioxide and isobutylene, both gasses that leave the coating. The deprotection reveals phenolic moieties, which are soluble in aqueous base, therefore this material can function as a *negative tone photoresist*.



Interestingly, poly(ϵ -Boc styrene) can *also* work as a *positive tone photoresist* by using another developing solvent. The unmodified, original polymer is soluble in nonpolar solvents, for example anisole, and can be selectively washed away to leave behind the more polar modified polymer, which is insoluble in anisole. However, the negative mode is more often used because of the low toxicity of the aqueous base developer.

As with Novolak, the key ingredient is the so-called *photochemical acid generator*. These compounds were developed by James Crivello (then with GE, now at RPI), and usually take the form of iodonium ($\text{R}_2\text{I}^+ \text{X}^-$) or sulfonium ($\text{R}_3\text{S}^+ \text{X}^-$) salts. These compounds decompose upon light exposure to provide a complicated mixture of products, chief among which is the acid HX . This acid then catalyzes the deprotection reaction of many ϵ -Boc groups.

Very fine features can be fabricated using this system, with very little light required to do the job.



Future Directions

- Industry is moving to ever shorter irradiation wavelengths (193 nm and then even lower) to get finer features.
- Aromatic-containing polymers are opaque at these short wavelengths, so new polymers and systems are required.
- Chemical amplification is essential to success.
- Environmental issues are increasingly important.
- Lots of research remains to be done (IBM, Bell Labs, Arch Corp, and many other labs)